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Dynamical nuclear polarization by means of shallow donors in ZnO quantum dots

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ABSTRACT

The almost complete dynamic nuclear polarization (DNP) of nuclear spins has been demonstrated can be achieved in ZnO and AgCl single crystals by saturating the EPR transition of the shallow donor (SD) present in this crystals with using high-frequency (275 and 95 GHz) at low temperatures. DNP effects have also been observed in ZnO quantum dots (QD's) where polarization of ^{67}Zn nuclear spins in ZnO core and of ^{1}H nuclear spins in the $Zn(OH)_2$ capping layer have been obtained by saturating the EPR transition of the SD present in the ZnO QD's. DNP manifests itself via a shift of the EPR lines of SD in bulk ZnO and AgCl crystals and the creation of a hole and an antihole in the EPR absorption line of the SD in QD's. The enhancement of the nuclear polarization opens the possibility to study semiconductor nanostructures with NMR techniques.

1. Introduction

High-frequency electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR) was shown to be a method of choice for investigation of shallow donors (SD) in wide-band-gap semiconductors (AgCl, ZnO, AlN) [1–4]. This is attractive spectroscopic techniques to identify dopants in single crystals and nanocrystals. Moreover by a study of the hyperfine (HF) interaction of the electron spin of this shallow donor with the nuclear spins as a function of the size of the nanocrystal, the effect of confinement on the spatial distribution of the electronic wave function could be measured.

During the EPR experiments on the Li-doped ZnO nanocrystals it was observed that prolonged irradiation of the EPR transition of this donor produces a hole in the EPR resonance line. It was suggested that this hole burning is caused by dynamic nuclear polarization (DNP) of the ^{67}Zn nuclear spins in the ZnO nanocrystal. In a subsequent publication this effect was studied in a bulk ZnO single crystal doped with H [5] which, in analogy to Li, also forms a shallow donor.

To investigate this problem we present here a study of the DNP process in ZnO nanoparticles with SD's using high-frequency EPR and ENDOR spectroscopy at low temperature. In addition we will spread our investigations of dynamic nuclear polarization on another system with shallow donors-AgCl crystals. Shallow donors in AgCl single crystals were investigated in detail in Ref. [1], it was identified the split-interstitial structure of the intrinsic shallow donors and the wave-function space distribution was measured up to about 60 shells.

We will suggest a possible explanation for the mechanism of the DNP process in the bulk crystals and nanoparticles. An attractive feature is that the enhancement of the nuclear polarization may open the possibility of studying semiconductor nanostructures with nuclear magnetic resonance (NMR) techniques that are usually difficult to apply in view of the small thermal polarization of the nuclear spins.

2. Experimental

Nominally undoped ZnO and AgCl single crystals were used. Free-standing ZnO nanocrystals with diameters of 2.8, 3.4, 4.0, and 4.2 nm were prepared via a wet chemical method [3]. The surface of the as-prepared dots is capped by a thin layer (about one monolayer) of $Zn(OH)_2$ and thus the dots consist of a ZnO/$Zn(OH)_2$ core-shell structure. The SD's were subsequently generated in AgCl and ZnO QD's by radiation from a 100 W mercury arc.

The EPR experiments were performed at temperatures ranging from 1.2 to 10 K using a pulsed EPR spectrometers operating at 275 and 95 GHz. The EPR spectra were recorded by detecting the

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